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Synthesis, spectral and thermal study of La(III), Nd(III), Sm(III), Eu(III), Gd(III) and Tb(III) complexes with mefenamic acid

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Abstract New binuclear complexes of La(III), Nd(III), Sm(III), Eu(III), Gd(III) and Tb(III) ions with mefenamic acid were obtained in solid phase. For all compounds considered, complexation occurs at pH 6–6.5. The analyzed complexes were characterized on the basis of chemical and elemental analyses, molar conductance, UV–Vis, IR and 1H NMR spectroscopies as well as thermoanalytical techniques. According to the research results, the molecular formula of the complexes is $Ln_2(C_{15}H_{14}NO_2)_3(OH)_3 \times nH_2O$, with the exception of the La(III) complex which has the formula $La_2(C_{15}H_{14}NO_2)_5(OH)$. The results show that only the carboxyl group is involved in the coordination of the rare earth ions in the bidentate mode. Coordination does not occur through the nitrogen atom. All the complexes are soluble in DMSO, and they are nonelectrolytes. The TG-FTIR technique was employed in order to study a decomposition pathway of the obtained compounds. The received results provide information on the composition, thermal stability, thermal decomposition, as well as the gaseous products that evolved during the thermal decomposition of the considered compounds.

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Introduction

Lanthanides present specific chemical, optical and magnetic properties that are a consequence of their peculiar electronic structure. Furthermore, when used in small quantities, they become essential to almost all aspects of modern life, from functioning as the active cores in catalysts for oil cracking, lighting devices, high-coercivity magnets used in motorization (electric cars, wind turbines, hard disk drives) or audio applications, lasers and telecommunications, to different areas as biomedical analyses and imaging or agriculture [1].

Many studies concerning the lanthanides and their interactions with biological systems are currently carried out in order to gain a better understanding of their functional roles in biology and medicine. Lanthanides have been suggested for the treatment of a series of diseases and for diagnosis through magnetic resonance imaging [2]. Recent studies have shown that lanthanides could act as scavengers of free radicals and therefore protect cells and tissues from oxidative stress-induced injury [3]. A coordination compound of rare earth and drug may exhibit higher biological activity than that of metal or ligand because of synergetic effects [4, 5].

Mefenamic acid (2-[N-(2,3-dimethylphenyl)amino]benzoic acid), presented in Fig. 1, belongs to the group of aromatic amino acids. This compound is of specific interest because of its biological activity—it is a potential inhibitor of prostaglandin synthesis, the presence of which is closely associated with inflammatory processes [6]. It also displays analgesic, anti-inflammatory, antipyretic, antioxidant and

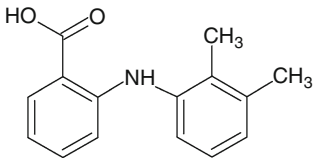

Fig. 1 Molecular structure of mefenamic acid

antiproliferative activity. Therefore, it is an important nonsteroidal drug used for treatment moderate pain of various origins (dysmenorrhea, rheumatic diseases, sciatica, headache, premenstrual syndrome, postoperative, posttraumatic and dental pains) [7, 8]. Also, mefenamic acid shows therapeutic effects as anticancer agent (particularly colon and liver cancer cell lines) [9, 10]. Furthermore, it is applied for the preparation of new potent anti-inflammatory and analgesic agents [11–13].

The biological activity of NSAIDs may be changed or improved due to the formation of metal complexes [14]. As long as mefenamic acid can form complexes with many metal ions, the formation of metal complexes plays important and multiple roles in biological systems. Metal-binding substances, many of which function by chelation, form a class of substances which have provided diverse useful drugs and other substances of value in selective toxicity. They have found many uses in veterinary and human medicine [15].

In recent years, new mefenamic acid complexes with metal ions have been synthesized and characterized for their potential applications in various fields. The complex of mefenamic acid with bismuth(III) [16] shows excellent in vitro activity against *Helicobacter pylori*, the bacterium which is mainly responsible for gastric, peptic and duodenal ulcers and gastric cancer [17, 18]. The complexes of mefenamic acid with Mn(II), Co(II), Ni(II), Zn(II) and Cu(II) show antioxidant properties and inhibitory effect against the soybean lipoxygenase [19]. Furthermore, the complex with Mn(II) exhibits the highest antioxidant and anti-inflammatory effect, and the complex with Cu(II) has antitumor activity comparable to that of a cisplatin. Also, Feng et al. [20] showed that three mefenamic acid complexes with Mn(II) obtained by them have a higher inhibitory activity against the lipoxygenase than the parent ligand, i.e., mefenamic acid. Additionally, the complexes of this amino acid with Ni(II), Zn(II) and Cu(II) demonstrate high affinity to bovine and human serum albumins [21–23].

It should be noted that, in most cases, the complexes are mononuclear (and synthetized with M:L ratios 1:1, 1:2, 1:3 and 1:4). Based on the study of mefenamic acid complexes with Fe(III) ions, it has been shown that mononuclear complexes were formed, but in the presence of an excess of Fe(III) ions, a binuclear complex was obtained [24]. Mononuclear complexes of mefenamic acid with rare earth elements have already been obtained by mixing ammonium mefenamate solution and appropriate rare earth chlorides or nitrates. Afterwards, they have been analyzed in order to introduce their physical, spectroscopic and thermal properties [25, 26]. Polynuclear metal complexes exhibit a fascinating variety of unusual symmetries and structural patterns [27]. The biological relevance of some of these compounds and their potentially important applications as advanced materials adds to their interest and significance [28]. Thus, our study has focused on the preparation of dinuclear complexes of mefenamic acid with La(III), Nd(III), Sm(III), Eu(III) Gd(III), and Tb(III) ions in the solid state, as well as on the analysis of their composition and properties by using elemental analysis, gravimetry, thermogravimetry, differential scanning calorimetry (DSC), IR and UV–Vis spectroscopy, molar conductivity, ^{1}H NMR spectroscopy and X-ray powder diffraction (XRD). We hope that the synthesis of these complexes will provide not only theoretical information on coordination chemistry, but also will give important information for further study of biological activities of these complexes as potential chemotherapeutic agents.

Experimental

Materials and measurements

Mefenamic acid and the rare earth(III) oxides (99.9 %) were obtained from Sigma-Aldrich. The rare earth(III) chlorides (1×10^{-2} mol dm^{-3}) were prepared by dissolving an appropriately weighted amounts of their oxides in concentrated hydrochloric acid ($d = 1.19$ kg dm^{-3}). The acid excess was evaporated, and the residues were dissolved in redistilled water. Methanol, sodium hydroxide and hydrochloric acid were acquired from POCH, Poland, while DMSO was from Merck. All the used chemicals were of analytical grade.

The contents of C, H and N in the complexes were determined with the usage of a Vario EL elemental analyzer. (Elementar, Germany). The metal content was determined by gravimetric method, and the water content was calculated on the basis of the results obtained by the thermogravimetric method. The chlorine content was determined by the Schöniger method. The FT–NMR spectrum for mefenamic acid and La(III) complex was recorded on a FT–NMR spectrophotometer, 500 MHz (Bruker). The UV–Vis spectra of the compounds in methanol and DMSO were performed with a V-670 UV–Vis–NIR spectrophotometer (Jasco, Japan). Infrared spectra were carried out in KBr pellets in 4000–400 cm^{-1} on an Alpha FT–IR spectrophotometer (Bruker, Germany). The

X-ray powder analysis of solid complexes samples was carried out by means of a Bruker D2 Phaser powder diffractometer, using Cu Kα radiation ($\lambda = 1.5406$ Å). The measurements were taken over the range of $2\theta = 10$–100°. Solubility study was carried out in methanol and DMSO at (20 ± 1) °C. Molar conductance at room temperature was measured in 1×10^{-3} mol/dm^3 DMSO solution using a CX-505 conductometer (Elmetron, Poland). Thermogravimetric analysis of the obtained lanthanide complexes was carried out using TGA/DSC1 apparatus (Mettler Toledo) in dynamic nitrogen atmosphere (50 mL min^{-1}) in the temperature range of 25–1000 °C at a heating rate 10 °C min^{-1}. Evolved gas analysis was also performed applying combined TG-FTIR technique. TG instrument was coupled with FTIR apparatus Nicolet iS10 (Thermo Scientific) by a transfer line heated at 220 °C. The differential scanning calorimetry (DSC) of the synthesized complexes was performed with a Mettler Toledo DSC–822e calorimeter in nitrogen atmosphere at a heating rate 10 °C min^{-1} from −30 to 250 °C.

Synthesis of the complexes

The synthesis of La(III), Nd(III), Sm(III), Eu(III), Gd(III) and Tb(III) complexes with mefenamic acid was carried out in aqueous–methanol solution according to the molar ratio of Ln^{3+} to ligand 1:2 at 70 °C under stirring. A stock solution of appropriate lanthanide ions (1×10^{-2} mol dm^{-3}) was added into a hot and saturated solution of mefenamic acid in methanol (1×10^{-2} mol/dm^3) and then diluted with water to the ratio of methanol to water 1:1. Afterwards, the pH of the mixture was adjusted to 6–6.5 by addition of 0.5 mol/dm^3 NaOH solution. The resulting solid complexes appeared as colored precipitates. The mixture was maintained at 60 °C for 1 h and then left at room temperature for 24 h. Next, the precipitates were filtered, washed with deionized water and methanol until no chloride ions could be found and finally dried in air at room temperature.

Results and discussion

Composition and physicochemical properties of the complexes

The composition of the obtained complexes was identified by elemental analysis, electronic and infrared spectra, thermogravimetric analysis and differential scanning calorimetry. The synthesized complexes have yellow–green color. They are insoluble in water and poorly soluble in other polar solvents (methanol, ethanol and acetonitrile). The solubility of the complexes in methanol is of the order of 10^{-5} mol dm^{-3}, with the exception of the lanthanum complex which is more soluble in methanol. In this case, the solubility value is about 10^{-4} mol dm^{-3}. All the compounds have a slightly greater solubility in DMSO (approximately 10^{-3} mol dm^{-3}).

The molar conductance of their 10^{-3} mol dm^{-3} DMSO solutions was varied from 14 to 34 Ω^{-1} cm^2 mol^{-1}, which indicates that the complexes are nonelectrolytes [29].

The XRD patterns (Fig. 2) show that only complex with La(III) ions has crystalline structure and other analyzed compounds are amorphous. The characteristic XRD peaks of the lanthanum complex are observed at 11.8°, 17.9°, 23.8° and 25.6° (2θ). These peaks are distinguished by one of the polymorphic forms of mefenamic acid (polymorph II) [30] as well as sodium and iron mefenamate [19].

Elemental analysis

The results of the chemical analysis and formulae of the prepared solid complexes are presented in Table 1. It was found that the composition of the lanthanum complex differs significantly from that of the other complexes.

The ease of hydrolysis of the lanthanide ions, and tendency to form a lanthanide–hydroxo species makes that suitable hydroxo complexes can be formed by reaction with organic ligand [31]. The studied complexes were formed in aqueous solutions at pH about 6.5 when in the solution both $Ln(OH)^{2+}$ and $Ln(OH)_2^+$ ions occur [32], so may be assume that the $Ln(OH)^+$ ions are present in the complex. Additionally, elemental analysis excluded the presence of chlorine in the obtained compounds. Therefore, the formula $La_2(C_{15}H_{14}NO_2)_5(OH)$ was proposed for La(III) complex and $Ln_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}nH_2O$ for the other complexes where Ln means Nd, Sm, Eu, Gd, Tb and

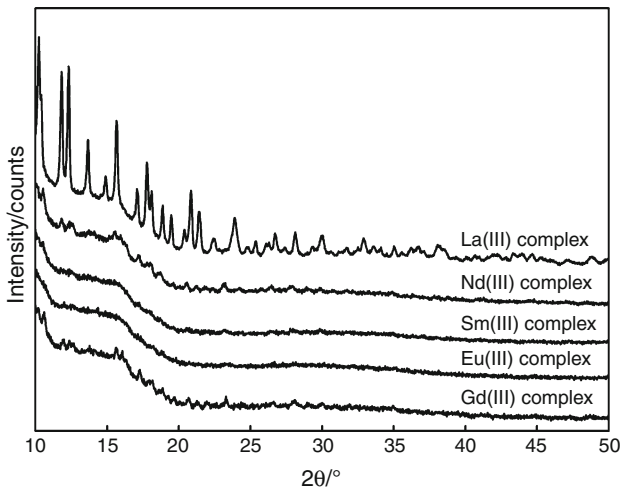

Fig. 2 X-ray powder diffraction patterns of Ln(III) complexes with mefenamic acid

Table 1 Results of chemical analysis and molar conductance data of Ln(III) complexes with mefenamic acid

Complex	Molecular mass/ g mol^{-1}	Mass fraction/% found (calculated)				Molar conductance/ Ω^{-1} cm^2 mol^{-1}
		Ln	C	H	N	
$La_2(C_{15}H_{14}NO_2)_5OH$	1469.19	17.98 (18.57)	59.76 (60.20)	4.78 (4.78)	4.62 (4.68)	34
$Nd_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}2H_2O$	1096.35	26.38 (26.31)	50.06 (49.30)	4.48 (4.51)	3.88 (3.83)	17
$Sm_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3H_2O$	1126.61	26.44 (26.69)	47.76 (47.97)	4.47 (4.56)	3.71 (3.73)	16
$Eu_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3.5H_2O$	1138.82	26.15 (26.48)	46.41 (47.46)	4.62 (4.60)	3.76 (3.69)	18
$Gd_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}.3H_2O$	1140.39	27.22 (27.58)	47.77 (47.39)	4.39 (4.51)	3.72 (3.69)	14
$Tb_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3H_2O$	1143.73	27.67 (27.79)	47.90 (47.25)	4.26 (4.49)	3.74 (3.67)	15

$n = 2$ for Nd, $n = 3$ for Sm, Gd and Tb as well as $n = 4$ for Eu.

UV–Vis study

The UV–Vis spectra of the mefenamic acid and the lanthanide complexes were recorded in methanol and DMSO. The spectral data are summarized in Table 2.

Figure 3 shows the absorption spectra of mefenamic acid and its europium complex in methanol and DMSO. The spectra of the other complexes were similar. The absorption spectrum of mefenamic acid is characterized by two bands: band I with maximum at around 350 nm and band II with maximum around 280 nm. The band I corresponds to $\pi \rightarrow \pi^*$ transition within the heterocyclic moiety (intramolecular hydrogen bonding ring) of the mefenamic acid molecule. The band II can be ascribed to $\pi \rightarrow \pi^*$ transition of the benzenoid system of mefenamic acid [33, 34].

The UV–Vis spectrum of mefenamic acid in DMSO is characterized by a slight bathochromic shift compared to the spectrum of this compound in methanol. The changes indicate that the excited states are more dipolar than corresponding ground states and, what is more, that electronic transition energy decreases, because the more dipolar excited state is stabilized by more polar solvent (DMSO) [35].

As regards the electronic spectra of the obtained complexes, the shifts of the characteristic bands were observed comparable to the ones of mefenamic acid, what confirms complex formation. The changes are very similar for all investigated complexes. Moreover, the influence of solvent polarity can be noted. The hypsochromic shift of the band I by 4–5 nm in methanol and 12–13 nm in DMSO was observed. The band II was shifted bathochromically by 5–6 nm in methanol and 13 nm in DMSO. In addition, the noticeable absorbance decrease of the band II in the spectra of the complexes in DMSO was observed. The study shows that the absorption spectra of the obtained complexes are

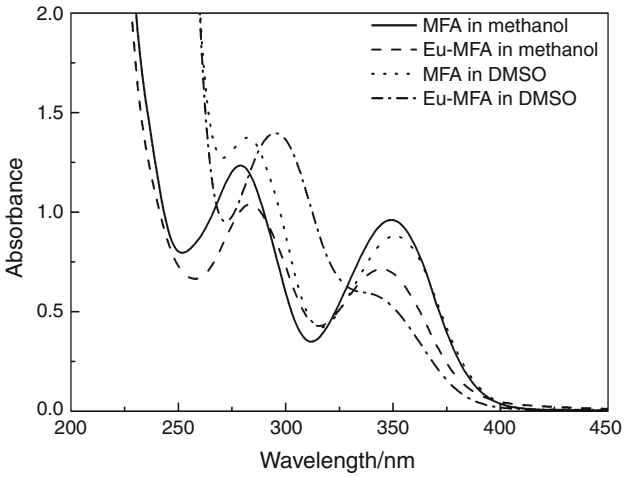

Fig. 3 Absorption spectra of mefenamic acid (MFA) and Eu(III) complex with mefenamic acid (Eu–MFA) in methanol and DMSO

Table 2 Spectral data ($\lambda_{max,}$ nm) of mefenamic acid and its complexes with Ln(III) ions in methanol and DMSO solutions

Solvents	MFA	Complex					
		La(III)	Nd(III)	Sm(III)	Eu(III)	Gd(III)	Tb(III)
Methanol	279	284	284	284	283	283	283
	349	344	345	345	345	345	345
DMSO	282	295	295	295	295	294	294
	351	338	338	338	338	338	338

determined by the coordinated organic ligand what is typical for lanthanide complexes [36].

IR spectra

The IR spectra provide valuable information regarding the nature of the functional group attached to the metal atom. The IR spectra of the six rare earth complexes and mefenamic acid were performed with KBr pellets in the range of 4000–400 cm^{-1} and have been used to define the structure of the synthetized compounds. They were interpreted on the basis of main bands of mefenamic acid and its complexes that are given in Table 3.

The IR spectra of all complexes are very similar; nevertheless, the comparison of these spectra with that of mefenamic acid shows important spectral changes (Fig. 4). Moreover, the IR spectra of all complexes are almost identical (slight differences concern the intensity of bands, not their location) with the exception of the spectrum of La(III) complex which differs significantly in the range of 3800–3400 cm^{-1}. In this region for Nd(III), Sm(III), Eu(III), Gd(III) and Tb(III) complexes, the broad envelope band with a high intensity appears. This indicates the presence of weak hydrogen bonds that stabilize the structure of the complexes [37, 38]. This band is connected with the presence of water in the obtained complexes, because it is the characteristic band for the OH stretching vibrations (asymmetric and symmetric) in water molecule. The presence of water in these complexes was confirmed by the thermal analysis. For La(III) complex, this band is slightly outlined.

The stretching vibrations of the NH group of mefenamic acid are observed at a wavelength of 3310 cm^{-1}, and for the synthesized complexes, only a small shift of this band toward higher frequencies is observed. Therefore, we concluded that nitrogen atom of the amino group does not participate in the coordination of the metal ion [15, 24, 39]. Examined spectra exhibit a band derived from asymmetric and symmetric stretching vibrations of methyl group observed at 2974–2858 and 2969–2859 cm^{-1} for mefenamic acid and complexes, respectively. In the spectrum of mefenamic acid, the broadband characteristic for OH stretching vibrations of the carboxyl group is observed in the range of 3300–2500 cm^{-1}, but in the spectra of complexes this band disappears.

It has been found that the greatest changes occurred in the frequency range in which the bands characteristic for the carboxyl group in mefenamic acid are present, i.e., the disappearance of the band assigned to the stretching vibrations of the carbonyl group at 1648 cm^{-1}. On the other hand, in the spectra of the complexes, two new bands appear at 1613–1614 and ~1390 cm^{-1}. They can be attributed to the asymmetric and symmetric stretching vibrations of the COO^- group, respectively. The IR band shift of the carbonyl group toward the smaller wavenumber is probably connected with the lengthening of the C–O bond in the carboxylate group, thereby a reduction in the force constant. The complexation may be the reason of this phenomenon. Presented data indicate that the COO^- group is involved in the coordination of the studied lanthanide ions. The differences ($\Delta\nu$) between the wavenumbers of asymmetric and symmetric stretching vibrations for the

Table 3 IR bands of mefenamic acid, sodium mefenamate [37] and Ln(III) complexes with mefenamic acid

Compound	$\nu_{(NH)}$	$\nu_{(COOH)}$	$\nu_{as(COO^-)}$	$\nu_{s(COO^-)}$	$\Delta\nu^*$	$\delta_{(NH)}$	$\nu_{(Ln-O)}$
Mefenamic acid	3310	1648			–	1576 1510	–
Sodium mefenamate			1612	1373	239		
$La_2(C_{15}H_{14}NO_2)_5(OH)$	3339	–	1614	1394	220	1579 1506	429
$Nd_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}2H_2O$	3305	–	1614	1390	224	1578 1497	435
$Sm_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3H_2O$	3310	–	1614	1394	220	1578 1497	437
$Eu_3(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3.5H_2O$	3318	–	1614	1398	216	1578 1497	437
$Gd_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3H_2O$	3315	–	1614	1398	216	1578 1497	439
$Tb_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3H_2O$	3335	–	1613	1397	216	1578 1497	440

* $\nu_{as(COO^-)} - \nu_{s(COO^-)}$

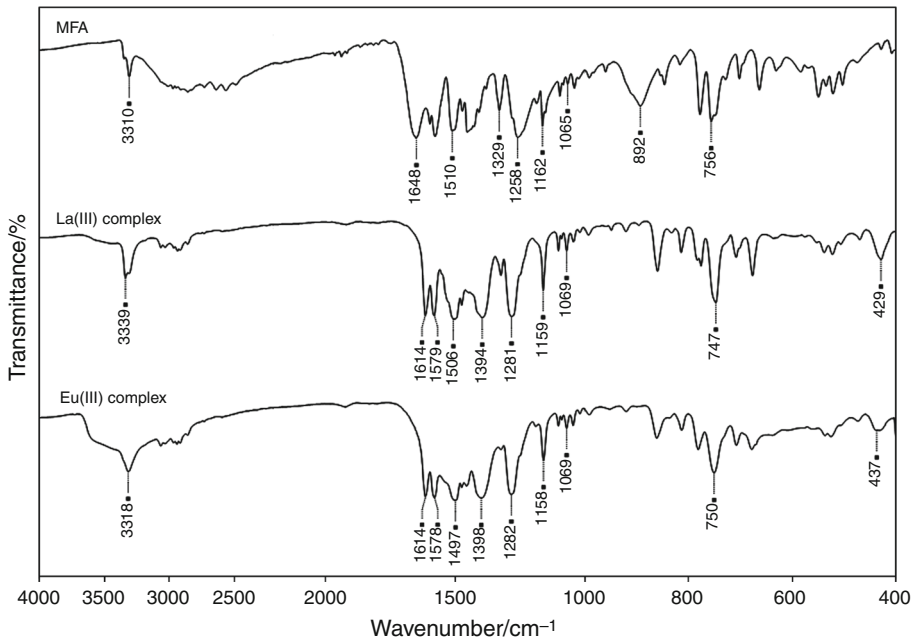

Fig. 4 FTIR spectra of mefenamic acid, La(III) and Eu(III) complexes with mefenamic acid

carboxylate group were calculated and compared with the value of $\Delta\nu$ obtained for sodium salt of mefenamic acid. In the case of NaMFA, the value of $\Delta\nu = 239$ cm^{-1} [40] and for the complexes the values of $\Delta\nu$ are about 220 cm^{-1}. Based on the value of $\Delta\nu$ for the obtained complexes, the monodentate type of the carboxylate group can be unambiguously excluded, while bidentate coordination is possible [41, 42]. The smaller $\Delta\nu$ values of the complex suggest the existence of the bridge-type or chelate-type bonding between the metal and ligand [39, 43]. Furthermore, taking into account the specific characteristics of dimeric and polymeric lanthanide complexes (due to their large number of coordination and the absence of a special preference for the coordination geometry), the mixed bridge–chelate-type bonding nature of the carboxylate group is also possible.

In the spectra of the complexes, the bands associated with the deformation CO–H, stretching C–O and bending OH (out of plane) vibration are not observed. Those bands are present in the spectrum of mefenamic acid at 1426, 1329 and 892 cm^{-1}, respectively.

In the low-frequency region of the complexes spectra, additional bands of medium intensity occur in the 420- to 440-cm^{-1} range and these bands could be assigned as metal–oxygen stretching vibrations. These sensitive bands exhibit a regular shift toward higher wavenumbers in the order from La(III) to Tb(III) complexes, which means that the stretching frequencies of Ln–O bonds increase with the increasing of atomic number in the series of lanthanide ions. Thus, the force constant of the lanthanide metal–oxygen bond also increases, which is due to the increase in covalency of the Ln–O bond in the obtained compounds [44].

^{1}H NMR spectra

^{1}H NMR spectra (recorded in DMSO-d_6 and in D_2O-DMSO-d_6 system) were acquired for mefenamic acid and the synthesized La(III) complex to investigate possible coordination modes. Assignments of the resonances of aromatic protons and protons in methyl groups of mefenamic acid were made by considering the available literature data [45]. Comparison of the ligand and the complex spectra revealed that the significant changes appeared only for the signals which are commonly assigned to the protons of carboxyl and amino group. In mefenamic acid spectrum recorded in DMSO-d_6 solution, the signals at 12.98 and 9.45 ppm correspond to mentioned protons, respectively. Disappearance of these signals in MFA spectra registered in D_2O-DMSO-d_6 system confirmed correct assignment.

In the spectrum of La(III) complex in DMSO-d_6 disappears the signal of the proton of carboxylate group and the signal of proton of amino group shifts to 10.27. The disappearance of proton signal of the COOH group in La(III) complex confirms the involvement of this group in the creation of the complex. The existence of the HN resonance in the ^{1}H-NMR spectra indicates that the nitrogen atom remains protonated in the obtained complex. The significant shift of NH proton can be attributed to the break of an intramolecular hydrogen bond between the carboxyl and amino groups that occurs in mefenamic acid molecule.

Thus, it can be concluded that La(III) complex with mefenamic acid was formed.

Thermal analysis

Thermal analysis of lanthanide complexes was performed in order to study the nature of water in the investigated compounds, their thermal stability, as well as decomposition modes under controlled heating rate. The measurements were taken in nitrogen atmosphere within 25–1000 °C at a heating rate of 10 °C min^{-1}.

The curves of TG, DTG and DSC for the particular compounds are shown in Fig. 5, whereas their interpretation is presented in Table 4.

The analysis of the TG and DSC curves demonstrates that they undergo gradual decomposition as the temperature increases. With the exception of the complex with lanthanum ion, where decomposition is a three-step process, all other complexes are characterized by four-step decomposition.

The first step of decomposition on the TG curves occurs within temperature range 30–190 °C and is centered at 85 °C (mass loss = 3.5 %), 80 °C (mass loss = 4.6 %), 58 °C (mass loss = 5.1 %), 59 °C (mass loss = 4.48 %) and 58 °C (mass loss = 4.6 %), respectively, for Nd(III), Sm(III), Eu(III), Gd(III) and Tb(III) complexes. This decomposition step is related to dehydration process and corresponds to the loss of two water molecules for neodymium complex, three molecules of water for samarium, gadolinium and terbium complexes and 3.5 molecules of water in the case of europium complex. For lanthanum complex, no peak on DTG curve in temperature range up to 350 °C is observed, indicating that the anhydrous compound was received.

Temperature range of dehydration as well as value of dehydration enthalpy can be used to study the nature of water in metal complexes [46, 47]. The presence of crystallization or coordination water has influence on the initial course of the process of thermal compounds decomposition. In order to establish the nature of water molecules in the obtained hydrated metal complexes additionally, the DSC technique was employed. Measurements were taken in temperature range from −30 to 250 °C. The broad, endothermic peaks are observed on the DSC curves obtained for complexes of Ln(III) with mefenamic acid for dehydration stage (Fig. 6). The results indicate that this process is a single step. Thus, in the synthesized compounds, one type of water molecules is present [48].

Based on the obtained data, the values of the dehydration enthalpy were calculated and the results are summarized in Table 5. The dehydration enthalpies per one water molecule found for investigated complexes are between 17 and 22 kJ. Low values of dehydration enthalpies indicate that the water molecules are weakly bonded to the ligand and probably participate in the formation of hydrogen bond with mefenamate ligand. Hence, the obtained lanthanide compounds contain only crystallization water molecules [49, 50].

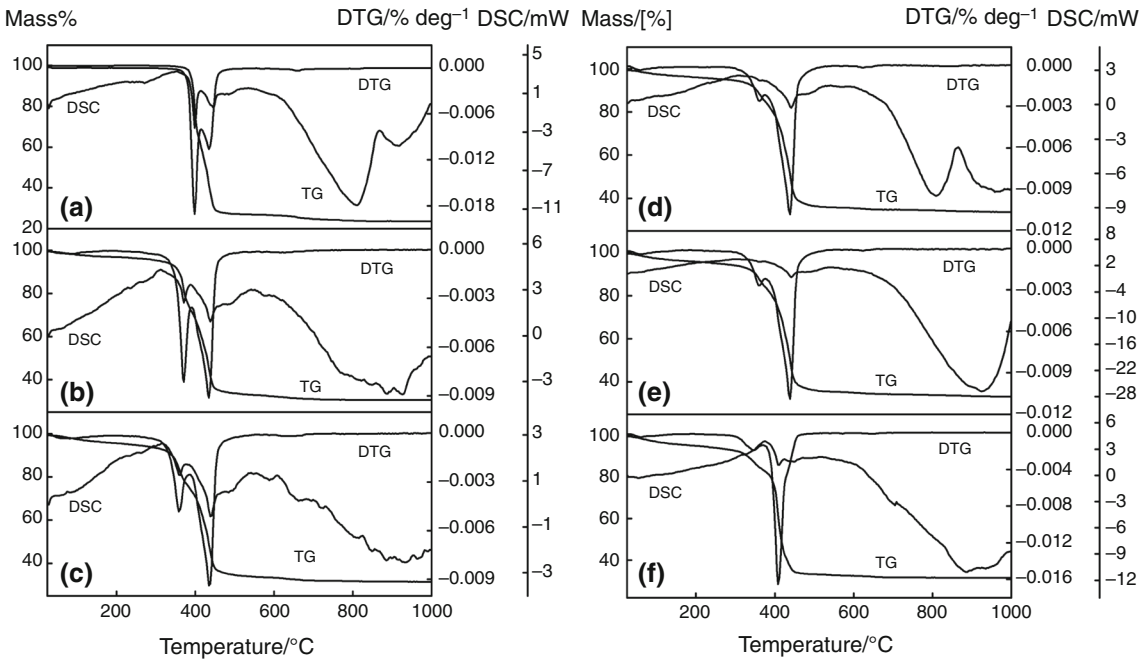

Fig. 5 TG, DTG and DSC curves for: (*a*) La(III), (*b*) Nd(III), (*c*) Sm(III), (*d*) Eu(III), (*e*) Gd(III), (*f*) Tb(III) complexes with mefenamic acid

Table 4 Thermal decomposition data for Ln(III) complexes with mefenamic acid in nitrogen atmosphere

Complex	Stage	Temperature range/°C	$T_{max.}^{DTG}$/°C	Δm/%	Residue/% found (calc.)
$La_2(C_{15}H_{14}NO_2)_5(OH)$	I	30–410	399	39.7	23.2 (22.2)
	II	410–590	436	35.3	
	III	590–1000	660	3.0	
$Nd_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}2H_2O$	I	30–180	85	3.5	29.4 (28.6)
	II	180–390	372	26.1	
	III	390–520	436	40.6	
	IV	520–1000	626	2.8	
$Sm_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3H_2O$	I	30–190	80	4.6	30.8 (31.7)
	II	190–390	360	21.1	
	III	390–550	437	41.1	
	IV	550–1000	644	2.4	
$Eu_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3.5H_2O$	I	30–180	58	5.1	31.4 (30.7)
	II	180–370	346	11.9	
	III	370–570	410	50.4	
	IV	570–1000	798	1.2	
$Gd_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3H_2O$	I	30–130	59	4.5	32.0 (32.5)
	II	130–380	361	13.0	
	III	380–550	439	48.2	
	IV	550–1000	625	2.3	
$Tb_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3H_2O$	I	30–190	58	4.6	33.9 (33.4)
	II	190–380	361	11.3	
	III	380–550	439	48.1	
	IV	550–1000	625	2.1	

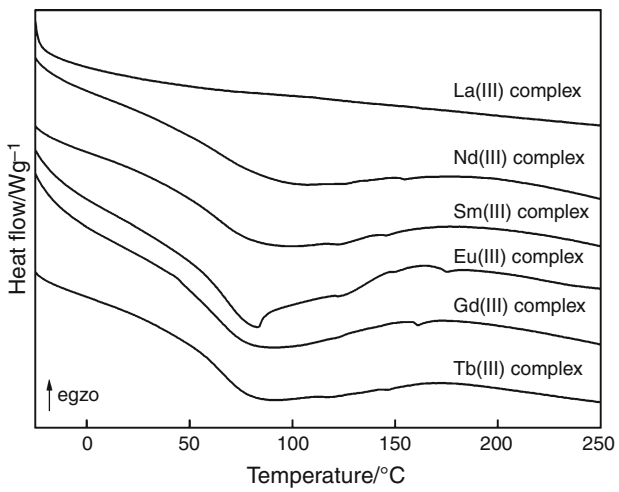

Fig. 6 The DSC curves for dehydration stage obtained for the complexes of Ln(III) with mefenamic acid

After dehydration step, the resulting anhydrous compounds are stable up to about 350 °C. It is confirmed by plateau observed on TG curves up to 350 °C. The next decomposition steps for investigated compounds are connected with the degradation of Ln–OH bonds and the decomposition of their organic part. Also, the literature studies show that the OH groups can be released at higher temperatures than the dehydration is observed and this process may be connected with the decomposition of the organic part of the complex [51, 52].

With regard to europium complex, in the first stage of organic part decomposition, the exothermic effect is observed, while the second stage is connected with endothermic peak on DSC curve. For neodymium, samarium, gadolinium and terbium complexes, both stages of organic part decomposition are connected with endothermic peaks on DSC curves. For europium complex, the temperature of maximum mass loss (T_{max}^{DTG}) at first and second stages of organic part degradation is observed at about 350 and 410 °C, whereas for Nd, Sm, Eu, Gd and Tb complexes at 360 and 440 °C, respectively. Second stage of organic part decomposition is related to the largest mass loss that for Eu(III), Gd(III) and Tb(III) complexes achieves about 50 % of initial sample mass. In the case of lanthanum complex, degradation of organic component is connected with two endothermic peaks on DTG curve with T_{max}^{DTG} at 400 and 440 °C and slightly larger mass loss is

Table 5 Thermoanalytical data for dehydration processes of the complexes of Ln(III) with mefenamic acid

Complex	Dehydration temperature range (DSC)/°C	Peak temperature (DSC)/°C	Dehydration enthalpy/kJ mol^{-1}	Mass loss/% found (calc.)
$Nd_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}2H_2O$	30–180	95	34.5	3.5 (3.3)
$Sm_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3H_2O$	30–190	86	51.9	4.6 (4.8)
$Eu_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3.5H_2O$	30–180	83	77.8	5.1 (5.5)
$Gd_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3H_2O$	30–130	81	49.5	4.5 (4.7)
$Tb_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}3H_2O$	30–190	83	53.3	4.6 (4.7)

observed at the first step of organic part degradation than for the second one.

Small peaks on DTG curves in the temperature range of 500–700 °C are noted for lanthanum, neodymium, samarium, gadolinium and terbium complexes. These peaks are associated with samples mass loss of about 2 % (and 3 % for La complex), what may suggest that the formation of final products of decomposition is preceded by the formation of unstable intermediate product. In case of lanthanide complexes, the formation of unstable oxycarbonates is observed [25, 53].

The solid residues obtained during thermal decomposition of Sm(III) and Gd(III) complexes are suitable to metal oxides: Sm_2O_3 and Gd_2O_3. On the other hand, in case of La(III), Nd(III) Eu(III) and Tb(III) compounds, the solid residue masses are higher than expected for metal oxides. It suggests that the decomposition of mentioned complexes in nitrogen atmosphere leads probably to appropriate metal oxide (La_2O_3, Nd_2O_3, Eu_2O_3 and Tb_4O_7) and carbon as final products, what is characteristic for investigations carried out in N_2 atmosphere [42].

Evolved gas analysis during thermal decomposition in nitrogen

FTIR spectra of evolved gas products of the thermal degradation were recorded for La(III) and Nd(III) complexes as representatives of the isostructural groups of the investigated compounds. The spectra of gaseous species of decomposition for those complexes were very similar. Stacked plots of FTIR spectra of gaseous species, made for the mefenamic acid complexes with La(III) and Nd(III) during their thermal decomposition in nitrogen, are shown in Fig. 7.

On the FTIR spectra of the evolved gases, several characteristic bands can be distinguished. The bands in the wavenumber ranges of 3750–3500 and 1900–1300 cm^{-1} correspond to vibrations of water molecules. The strong bands in the range of 2400–2300 and 700–600 cm^{-1} are characteristic vibrations for carbon dioxide, and they correspond to asymmetrical stretching and degenerate

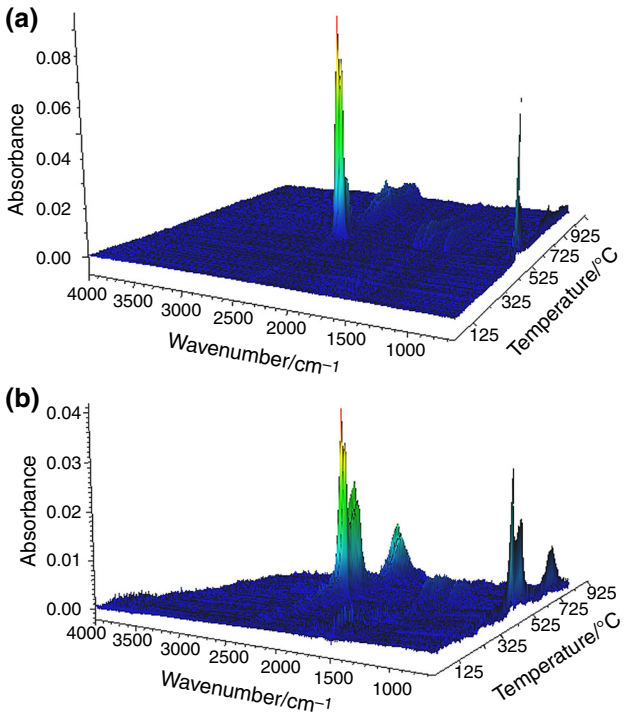

Fig. 7 Stacked plot of the FTIR spectra of the evolved gases for: **a** La(III) complex, **b** Nd(III) complex

bending vibrations, respectively. Moreover, the combination of those vibrations can give bands above 3500 cm^{-1} for CO_2 [54]. The presence of hydrocarbon compounds in gaseous products can be also confirmed by the presence of the bands in the range of 3300–2800, 1600–1585, 1500–1400, 1250–1000 and 900–675 cm^{-1}. Taking into account the ligand structure, one may assume that the band above 3000 cm^{-1} with peak at 3057 cm^{-1} is due to valence CH vibrations in aromatic hydrocarbons. The band below 3000 cm^{-1} with maximum at 2936 cm^{-1} is associated with the asymmetric and symmetric stretching vibrations of methyl group. Bands at 1590, 1498, 1073 and 743 cm^{-1} are typical for benzene ring. They correspond to the stretching CC, in-plane CH bending deformation and out–of–plane CH bending deformation vibrations, respectively [55].

FTIR spectra of gaseous species produced for La(III) and Nd(III) complexes during their thermal decomposition in nitrogen in different temperature are presented in Fig. 8.

These spectra confirm that the initial sample heating is connected with the release of water. Two-step process of organic part decomposition is accompanied mainly with the release of carbon dioxide and hydrocarbon compounds. The maximum of carbon dioxide emission is observed at ca. 405 and 372 °C for La(III) and Nd(III) complexes, respectively. The release of CO_2 above these temperature values gradually decreases. However, slight increase of the carbon dioxide emission in the temperature value at ca. 600 °C suggests that the decomposition of intermediate products, possibly oxycarbonates, occurs.

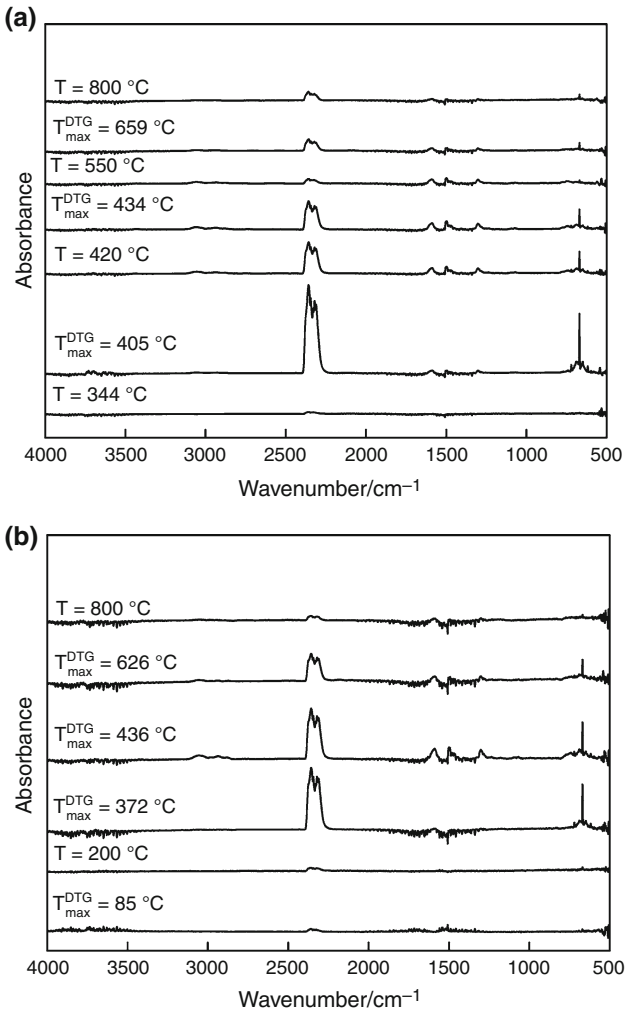

Fig. 8 The FTIR spectra of the evolved gases produced during thermal decomposition in nitrogen atmosphere at different temperatures of **a** La(III) complex, **b** Nd(III) complex

Conclusions

In this paper, the study of the synthesis, structure and physicochemical properties of the complexes of mefenamic acid with some lanthanide(III) ions is presented. We have found that in aqueous–methanol solutions and at pH 6–6.5 La(III) ions form with mefenamic acid solid complexes having the following formula: $Ln_2(C_{15}H_{14}NO_2)_3(OH)_3{\cdot}nH_2O$, where Ln is the trivalent cation of lanthanide and $n = 2$ for Nd(III), $n = 3$ for Sm(III), Gd(III) and Tb(III) as well as $n = 4$ for Eu(III).

The complex with Ln(III) ions has the composition significantly different from the other complexes, and its formula is $La_2(C_{15}H_{14}NO_2)_5(OH)$ and does not contain water.

The IR and ^{1}H NMR spectroscopic data for the obtained compounds confirm that the Ln(III) ions are coordinated to the ligands by the oxygen of the carboxylate group. However, the crystallographic studies are also necessary in order to accurately examine their structures. This is the purpose of the present and further authors' research.

The XRD patterns show that the complex with La(III) ions has crystalline structure and other analyzed compounds are amorphous.

Thermal studies clearly indicate that thermal decomposition of the investigated compounds in nitrogen atmosphere is four-step process with the exception of the complex with La(III) ions where the decomposition is a three-step process.

The first step of decomposition of the Nd(III), Sm(III), Eu(III), Gd(III) and Tb(III) complexes in nitrogen atmosphere is related to dehydration process. For La(III) complex, no peak on DSC curve is observed in temperature range from −30 to 250 °C, indicating that this compound is anhydrous. On the DSC curves obtained for the other complexes the broad, endothermic peaks are observed; thus, in these compounds one type of water molecules is present. The low values of dehydration enthalpies indicate that these compounds contain only crystallization water. The next decomposition steps for investigated compounds are connected with the degradation of Ln–OH bonds and the decomposition of their organic part. The final solid residues are suitable metal oxides or mixture of metal oxides and carbon, what is characteristic for investigations carried out in nitrogen atmosphere.

The TG-FTIR technique provided unreported information concerning the gaseous products that evolved during thermal decomposition in nitrogen atmosphere. The monitoring of the evolved gases during the thermal degradation in dynamic nitrogen atmosphere confirmed that water, carbon dioxide and aromatic hydrocarbons were main products of the decomposition of the obtained complexes.

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